ENVIRONMENTAL LIFE CYCLE ASSESSMENT OF CADMIUM TELLURIDE SOLAR CELLS: Cd EMISSSIONS

Vasilis M. Fthenakis
[1] National Photovoltaic Environmental Research Center, Department of Environmental Sciences,
Brookhaven National Laboratory, Upton, NY 11973
*email: vmf@bnl.gov; tel. (631)344-2830; fax (631)344-4486

ABSTRACT: This analysis focuses on cadmium flows and atmospheric emissions in the life cycle of cadmium telluride solar cells. New data in the mining/smelting and utilization phases were used. Published estimates were cross-referenced with current environmental impact reports from metal smelting facilities, and experimental investigations were conducted to quantify emissions during fires. It was estimated that the total of atmospheric emissions of cadmium during all the phases of the modules' life is about 0.02 g of Cd per GWh of electricity produced. These life-cycle emissions are two orders of magnitude lower than the controlled routine Cd emissions during the operation of modern coal-fired power plants.

   Keywords: CdTe, Environmental Effect, Manufacturing and Processing

1 INTRODUCTION

This assessment focuses on cadmium flows and emissions in the "cradle to grave" life cycle of cadmium telluride solar cells. It examines only the photovoltaic compounds (i.e. CdTe and CdS); other materials in the PV module (e.g., glass, EVA, metal contacts) are generic to all technologies and are not included. The prime focus is on cadmium flows and cadmium emissions in the environment. The life-stages of the cadmium compounds involve:1) production of raw materials (Cd and Te), 2) purification of Cd and Te, 4) production of CdTe, 5) manufacture of CdTe PV modules, 6) use of CdTe PV modules, and 7) disposal of spent modules. A detailed description of these phases can be found in a recent review article [1].

2. CADMIUM PRODUCTION

2.1 Mining

CdTe is manufactured from pure Cd and Te, both of which are byproducts of smelting prime metals (e.g., Zn, Cu, Pb, and Au). Cadmium minerals are not found alone in commercial deposits. The major cadmium-bearing mineral is sphalerite (ZnS), present in both zinc and lead ores. Cadmium is generated as a byproduct of smelting zinc ores (~80%), lead ores (~20%), and, to a lesser degree, of copper ores.

Zinc ores contain 3% to 11% zinc, along with cadmium, copper, lead, silver and iron, and small amounts of gold, germanium, indium, and thallium.   The mean Cd concentration in the zinc ores is about 220 ppm. The concentration of zinc in the recovered ore (called beneficiating) is done by crushing, grinding, and flotation processes (Figure 1). These activities, if not adequately controlled could generate significant levels of dust. However, ASARCO and Cominco, two major metal producers, report that implement controls which minimize dust emisons. All of the mining, crushing, and grinding takes place underground and wet scrubbers and dry cyclones are utilized to collect the dust. Cominco uses a wet grinding proces resulting in a slurry from which,

reportedly, there are essentially no dust emisions [2]. Based on these reports and the range of emissions reported in the literature, we determined that controlled emissions during mining are about 30g of dust per ton ore.
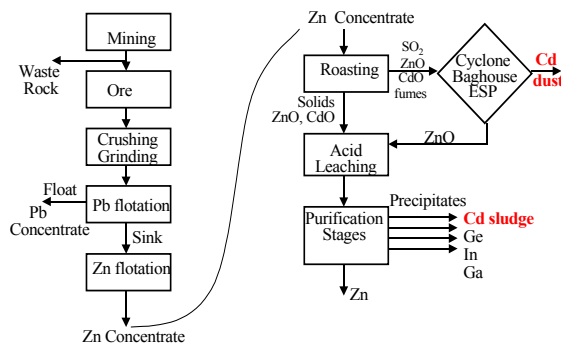

Fig. 1. Cd Flows in Zn mining and smelting

2.2 Smelting/Refining

The zinc and lead concentrates are transferred to smelters/refiners to produce the primary metals; sulfuric acid and other metals are frequent byproducts from most smelters. In addition to Zn, the mines in the United States also produce 100% of the Cd, Ge, In, and Th, 10% of Ga, 6 % of Pb, 4% of Ag and 3% of Au used in the country [3]. Since economic growth has steadily increased the demand for zinc for decades, impure cadmium is produced, regardless of its use.   Before cadmium production started in the United States in 1907, about 85% of the Cd content of the zinc concentrates was lost in roasting the concentrate, and in the fractional distillation of Zn metal [4].   Zinc can be refined by either pyrometallurgical or hydrometallurgical treatment of its concentrates. The four primary zinc-smelting operations of the United States use electrolytic technology [5]. Older roast/retort smelters are no longer employed in North America and Northern Europe. Berdowski et al. [6] reported on the emissions from zinc-smelting operations in several countries. Cd emissions vary widely depending on the ore used and the abatement measures applied. The

shift from pyrometallurgical to electrolytic processing has drastically reduced cadmium emissions (Table 1). The most recent data show 0.2 g Cd per ton of Zn product for North American and European Union countries [6, 7]. This numbers agrees with the emisssions reported for 2002 in one of the largest smelters of the world, the Trail, Canada Teck Cominco facility [8]. The air emissions of Cd in this facility have reportedly decreased by 84% between 1999 and 2002. The electrolytic zinc process consists of five main operations, roasting, leaching, purification, electrodeposition and melting/casting. Details of these operations can be found elsewhere [1].

Table 1. Cadmium Emissions from Old and New Zinc-Production Processes

Process	Cadmium Emissions	
	g Cd /ton Zn	(% Cd Loss)
Roast/leach/ electrowinning	0.2	(0.008 %)
Roast/blast furnace smelting (replaced in Canada & Europe)	50	(2 %)
Roast/blast furnace smelting (not in use any more)	100	(4 %)

The feed material for producing cadmium consists of residues from the electrolytic production of zinc, and of fume and dust, collected in baghouses from emissions during roasting [5]. Wastewater produced from leaching, purification and electrowinning usually is treated and re-used, with a small fraction of it discharged. Solid wastes include slurries from the sulfuric-acid plant, sludge from the electrolytic cells and copper cakes, and the byproducts of zinc production from the purification cells which contain cadmium, germanium, indium, and other metals. Purification byproducts and other solid wastes are recycled or stockpiled until they can be economically used.

Thus, Cd is a byproduct of zinc and lead and is collected from the emissions and waste streams of these major metals. Emissions in joint production of metals are allocated according to the International Standard Organization procedure ISO 14041, in proportion to the mass output or to the economic output of Zn, Cd, Ge and In from the smelters. The allocation to Cd ranged was 0.50% and 0.58% depending on the criterion employed [1]. These percentages are applied to emissions from mining and smelting, whereas, in the subsequent steps, 100% of the emissions are allocated to cadmium.

2.3 Cadmium Production from Zinc Electrolyte Purification Residue

The cadmium sponge, a purification product from precipitating zinc sulfate solution with zinc dust at the zinc smelter, is 99.5% pure cadmium. This sponge is

transferred to a cadmium recovery facility where it is oxidized in steam. Cadmium oxide, the product, is leached with spent cadmium electrolyte and sulfuric acid to produce a new recharged electrolyte. Impurities are precipitated with a strong oxidizing agent. The cathodes are removed once a day and are rinsed and stripped. The stripped cadmium is melted under flux or resin and cast into shapes. In a slightly different route, purification residues from the oxide and the sulfide-leaching processes are further leached with sulfuric acid and filtered through three stages to remove zinc, copper, and thallium before recovering the dissolved cadmium. Cadmium can be further purified with vacuum distillation to 99.9999% purity [8].

2.4. Purification of Cadmium and Production of CdTe

Metallurgical grade (i.e., 99.99% pure) metal is used in all current applications except for semiconductor materials that require higher purity. Purification residues from leaching plants undergo additional leaching with sulfuric acid and are filtered though three stages to remove zinc, copper, and thallium. The final step is vacuum-distillation [8]. High purity Cd and Te powders from other manufacturers are produced by electrolytic purification and subsequent melting and atomization (Figure 2), or by vacuum distillation.
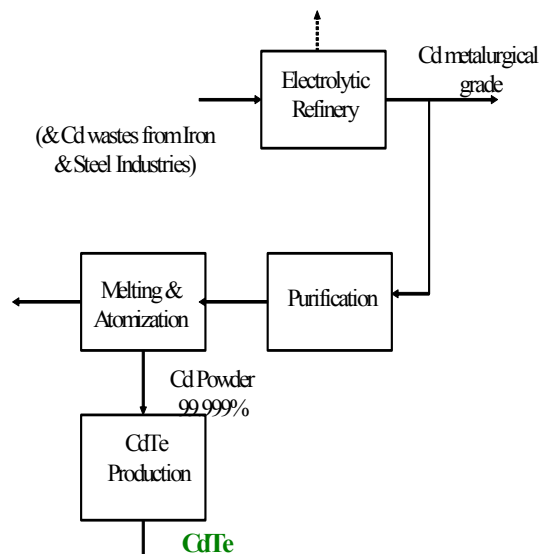
Fig. 2. Cd Flows from Cd Concentrates to CdTe

Both methods are proprietary and information about emissions is not published. Electrolytic purification does not produce any gaseous emissions. The melting and atomization steps needed to form the powder produce about 2% emissions that are captured by HEPA filters.

The efficiency of HEPA filters in collecting particulates of mean diameter of 0. 3 μm is 99.97%.

3. MANUFACTURING OF CdTe PHOTOVOLTAICS

Currently, the leading methods of making CdTe/CdS thin films is high-rate vapor transport, in which CdTe and CdS are deposited from the compounds in powder form after vaporization in a close-spaced reactor. The current material utilization rates range from 35% to 70%, but higher utilization rates are expected in optimized scaled-up production. Most of the unused vapors condense on the reactor's walls or rollers from where they are removed periodically; recycling of the residuals is both feasible and economic. Approximately 1% of the vapors are carried in the exhaust stream; these are collected at 99.97% efficiencies[1] using HEPA filters. The controlled Cd emissions correspond to 6 g per ton of Cd used in CdTe feedstock.

4. OPERATION OF CdTe PV MODULES

Thin-film α-Si, CdTe, and CIGS solar cells are durable and do not produce any emissions during extreme conditions of accelerated aging in thermal cycles from +80 ^{o}C to -80 ^{o}C [9]. Every PV generation, regardless of technology, is a zero-emissions process. Emissions could only be produced accidentally, if the metals are emitted during a fire. The fire effect on glass-to-glass encapsulated CdTe modules was recently investigated with emissions analysis and synchrotron x-ray fluorescence microprobe analysis of the molten glass and the results are presented by Fthenakis et al. in paper 5BV.1.32 of this conference. In these experiments CdTe was captured in the molten glass and almost none (~0.04%) was released.

5. END-OF-LIFE DISPOSAL OR RECYCLING

PV modules are expected to last 25 to 30 years. Should the modules at the end of their useful life end up in municipal landfills or incinerators, heavy metals could be released into the environment. CdTe PV modules that pass leaching criteria for non-hazardous waste could be disposed of in landfills, according to current laws. The leachability of metals in landfills currently is characterized by elution tests such as the US-EPA Toxicity Characterization Leachate Profile (TCLP), and the German DEV S4 (Deutsches Einheitsverfahren). Previous studies showed that PV recycling is technologically and economically feasible, although complete separation of Cd from the other metals of the module has not been accomplished yet [10,11]. Metals from used solar- panels in large centralized applications can be reclaimed in metal-smelting facilities, which use glass as a fluxing agent and recover most of the metals by incorporating them into their product streams. For dispersed operations and small-scale recycling, hydrometallurgical separations are economical [12]. A valid assumption is that CdTe PV modules will be either recycled or properly disposed off at the end of their

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[1] For particles of 0.3 μm or larger

useful life; therefore atmospheric emissions during/after decommissioning will be zero. Even if pieces of modules inadvertently make it to a municipal waste incinerator, cadmium will likely dissolve in the molten glass and would become part of the solid waste.

6. DISCUSSION

Our most likely estimates of atmospheric cadmium emissions during all the phases of the life of CdTe PV modules are shown in Table 2.

Our reference estimate of total air emissions is 0.02 g Cd/GWh of electricity produced, which is 25 times lower than the estimate (i.e., 0.5 g Cd/GWh] reported in an early study [13]. The main contributor to Cd air emission in the later assessment was PV utilization, under the assumption of Cd loss during fires. However, recent experimental tests proved that Cd is not emitted during fires. Also, our assessment uses more up-to-date assumptions and detailed calculations for determining emissions during mining, smelting/refining, and decommissioning of end-of-life products. It is interesting to compare Cd flows in CdTe PV with those in Ni-Cd batteries and coal-burning power plants. These comparisons are given in [1] and are summarized below:

Cadmium in Ni-Cd batteries is in the form of Cd and Cd $(OH)_2$, materials which are less stable and more soluble than CdTe. Based on data from the NiCd battery industry, a battery would produce an average of 0.046 kWh per g of its weight, which corresponds to 0.306 kWh per g of Cd contained in the battery. This is a 2500 times lower efficiency in using Cd than in a CdTe PV module.

Coal and oil-burning power plants, routinely produce Cd emissions (since Cd exists in both coal and petroleum), whereas CdTe PV does not emit anything during operation. According to data from the U.S. Electric Power Research Institute (EPRI), under the best/optimized operational and maintenance conditions, burning coal for electricity releases into the air generates a <u>minimum</u> of 2 g to 7.2 g of Cd per GWh (assuming well-maintained electrostatic precipitators or baghouses operating at 98.6% efficiency, and median concentration of Cd in US coal of 0.5 ppm (median) and 1.8 ppm (average) [14]. It is noted, that although very high effectiveness is expected for ESPs operating in North American Western European and Japanese power plants, ESPs are much less effective, if they are installed at all, in developing, coal-burning countries. In addition, 140 g/GWh of Cd inevitably collects as fine dust in boilers, baghouses, and ESPs, thereby posing occupational health- and environmental-hazards. Furthermore, a typical US coal-power plant emits per GWh about 1000 tons of CO_2, 8 tons of SO_2, 3 tons of NOx, and 0.4 tons particulates.

A last point is that cadmium is produced anyway as a byproduct of zinc production, and it can either be put to *beneficial* uses or *discharged* into the environment. When the market does not absorb the Cd generated by metal

smelters/refiners, it is cemented and buried, stored for future use, or disposed of to landfills as hazardous waste. Arguably, encapsulating cadmium as CdTe in PV modules is much more environmentally-friendly than all its current uses and disposal.

Table 2. Atmospheric Cd Emissions from the Life-Cycle of CdTe PV Modules

Process	Total Emissions (g Cd/ton Cd*)	Allocated Air Emissions		
		(g Cd/ton Cd)	(mg Cd/m2)	(mg Cd/GWh)
1. Mining of Zn ores	2.7	0.0157	0.0001	0.02
2. Zn Smelting/Refining	40	0.2320	0.0016	0.30
3. Cd purification	6	6	0.042	7.79
4. CdTe Production	6	6	0.042	7.79
5. CdTe PV Manufacturing	3	3	0.021	3.90
6. CdTe PV Operation	0	0	0.0003	0.06
7. CdTe PV Disposal/Recycling	0	0	0	0.00
TOTAL EMISSIONS		15.25	0.11	20.40

*ton of Cd used in manufacturing
Assumptions:
1. Mining of zinc ores produces 3 g of dust per ton of ore
2. Smelting/refining of Zn produces 0.2 g of Cd per ton of Zn production
3. The ratio of Zn to Cd content of Zn ores is 200
4. The mean concentration of Cd in Zn ores is 220 ppm
5. Emissions allocation to Cd in mining/smelting is 0.58% [1]
6. HEPA filters have a 99.97% effectiveness in collecting submicron size particulates in PV manufacturing exhaust streams
7. Emissions per module area and energy output are based on:
    7 g Cd/m^2 module; 10 % Electric conversion PV efficiency; Average US insolation (1800 kWh/m2/yr); 30 yrs PV module life expectancy, thus; 1 kg Cd produces 0.77 GWh over its life-time in PV.

7. REFERENCES

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